

# Doping asymmetry problem in ZnO: current status and outlook

A review of experimental and theoretical efforts focused on achieving p-type ZnO suitable for light-emitting optoelectronic devices for the blue/ultraviolet spectral range.

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**Abstract**—ZnO has gained considerable interest recently as a promising material for a variety of applications. To a large extent, the renewed interest in ZnO is fuelled by its wide direct band gap (3.3 eV at room temperature) and large exciton binding energy (60 meV) making this material, when alloyed with *e.g.* Cd and Mg, especially attractive for light emitters in the blue/UV spectral region. Unfortunately, as with other wide-gap semiconductors, ZnO suffers from the doping asymmetry problem, in that the *n*-type conductivity can be obtained rather easily, but *p*-type doping proved to be a formidable challenge. This doping asymmetry problem (also dubbed as the *p*-type problem in ZnO) is preventing applications of ZnO in light-emitting diodes and potential laser diodes. In this article, we provide a critical review of the current experimental efforts focused on achieving *p*-type ZnO and discuss the proposed approaches which could possibly be used to overcome the *p*-type problem.

**Index Terms**—ZnO, *p*-type, impurities, point defects

## I. INTRODUCTION

Unique optical and electronic properties, such as direct wide band gap of 3.3 eV at room temperature, high exciton binding energy of 60 meV, and possibly high radiation hardness make ZnO an attractive material for many device applications, such as light emitters and detectors, transparent thin-film transistors, highly conductive transparent oxides, gas sensors, *etc.* [1]–[3]. While some of these devices can be realized in ZnO with unipolar conduction, attainment of ZnO-based light-emitting devices utilizing electrical injection hinges on having both high quality *n*- and *p*-type ZnO with free-carrier concentrations well in excess of  $10^{17} \text{ cm}^{-3}$ , preferably in the  $10^{18} \text{ cm}^{-3}$  range. The prerequisites for “useful” *p*-type ZnO are for the acceptor concentration to be much higher than the donor concentration (low compensation), and low acceptor ionization energy, preferably well below 0.2 eV in

the dilute limit. In order to achieve high substitutional acceptor concentration, the solid solubility of the particular acceptor impurity in mind must be high with a low self compensation ratio.

Although ZnO undoubtedly has found and continue to find its way into some applications that are based on unipolar conduction, such as varistors [4], gas sensors [5] [6], transparent thin-film transistors [7]–[9], highly conductive transparent oxides as a less expensive/more abundant alternative to indium tin oxide (ITO) [10] [11], the lack of highly *p*-type conductivity continues to impede the development of ZnO-based light emitters. As stated, ZnO, as is the case for other wide-gap semiconductors, suffers from the doping asymmetry problem, in that it can be doped *n*-type rather easily, but *p*-type proved to be a formidable challenge which from a practical point of view has not been conquered yet. In general, the doping asymmetry arises from the fact that wide-gap semiconductors either have a low valence-band maximum or a high conduction-band minimum [12] [13]. Some semiconductors such as ZnTe, CdTe, and diamond in which the valence band is relatively close to the vacuum level have preferable *p*-type conductivity. Therefore, achieving *n*-type conductivity is very difficult, diamond being the case in point. In contrast, ZnO, ZnSe, ZnS, and CdS, which their valence bands relatively far from the vacuum level, have preferable *n*-type conductivity. Consequently, nominally undoped ZnO has *n*-type conductivity with a carrier concentration in bulk ZnO crystals varying from about  $10^{14}$  to mid- $10^{16} \text{ cm}^{-3}$ , and room-temperature mobility  $\mu_n \approx 200 \text{ cm}^2/\text{Vs}$  [14]. The source of this conductivity is due to intrinsic defects such as oxygen vacancies ( $V_O$ ) [15] [16] acting as deep donors, interstitial Zn ( $Zn_i$ ) [17] and Zn antisites ( $Zn_{O^{2+}}$ ) forming shallow donor levels [16], and background hydrogen acting as donor at interstitial sites [18]. Zn vacancies ( $V_{Zn}$ ) which have a low formation energy in *n*-type material are the dominant acceptors in the as-grown *n*-type ZnO as shown by positron annihilation spectroscopy [19]. To date, *n*-type doping is relatively well established through the substitution of group III elements (Al, Ga, In) on the Zn sites. Highly conductive *n*-type ZnO ( $n > 10^{20} \text{ cm}^{-3}$ ) can be produced by intentional doping (*e.g.*, see the review by Özgür *et al.* [1] and references therein). Unfortunately, the same intrinsic defects which are responsible

Manuscript received April 24, 2009

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Report Documentation Page			Form Approved OMB No. 0704-0188		
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1. REPORT DATE <b>APR 2009</b>		2. REPORT TYPE		3. DATES COVERED <b>00-00-2009 to 00-00-2009</b>	
4. TITLE AND SUBTITLE <b>Doping asymmetry problem in ZnO: current status and outlook. A review of experimental and theoretical efforts focused on achieving p-type ZnO suitable for light-emitting optoelectronic devices for the blue/ultraviolet spectral range.</b>				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S)				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) <b>Air Force Office of Scientific Research,Arlington,VA,22203</b>				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSOR/MONITOR'S ACRONYM(S)	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT <b>Approved for public release; distribution unlimited</b>					
13. SUPPLEMENTARY NOTES <b>U.S. Government or Federal Rights License</b>					
14. ABSTRACT <b>see report</b>					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT <b>Same as Report (SAR)</b>	18. NUMBER OF PAGES <b>11</b>	19a. NAME OF RESPONSIBLE PERSON
a. REPORT <b>unclassified</b>	b. ABSTRACT <b>unclassified</b>	c. THIS PAGE <b>unclassified</b>			

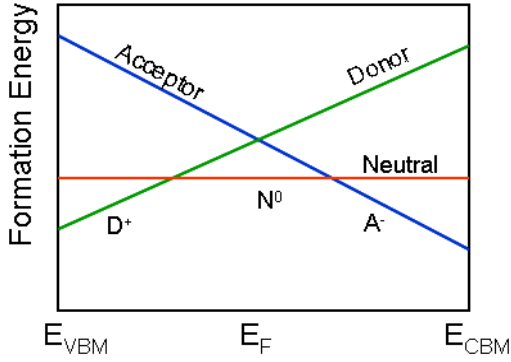


Fig. 1. Schematic dependence of the formation energy of charged defects on the Fermi energy position (courtesy of Y. F. Yan and S. H. Wei).

for *n*-type doping tend to aggravate the efforts to achieve *p*-type doping by compensating the potential acceptors.

In this manuscript, we critically review the experimental and theoretical efforts expended on overcoming the *p*-type problem in ZnO which is considered as the main obstacle to the development of ZnO-based optoelectronics devices. We first delve into the impediments in achieving a robust *p*-type ZnO in Section II. This is followed by a brief overview of the experimental efforts and the current status of the problem in Section III. Finally, strategies proposed recently which can be used to overcome the *p*-type problem are discussed in Section IV.

## II. ROADBLOCKS TO ACHIEVING P-TYPE ZnO

In general, there are three fundamental factors that raise obstacles to attaining *p*-type conductivity: (i) spontaneous formation of defects compensating *p*-type impurities, (ii) limited solubility of *p*-type impurities [20] and precipitate formation [21], and (iii) relatively deep acceptor levels [22] which remain unionized at operating temperatures. To make matters worse, the available data when scrutinized show instability of *p*-type conductivity in ZnO, reverting to *n*-type conductivity within a matter of days [23]. Furthermore, due to localization effects accompanying *p*-doping experiments, one should also be vigilant about the accuracy of *p*-type conductivity determination.

Among the above mentioned obstacles, the compensation problem is perhaps the most challenging one in wide-gap semiconductors in general and to a relatively large extent in ZnO. Fig. 1 shows schematically the general trends in the formation energies of charged compensating defects as a function of the Fermi level ( $E_F$ ) position [24]. Incorporation of donors or acceptors into semiconductors changes the  $E_F$  position, which can lead to spontaneous formation of the compensating charged defects. For instance, when a semiconductor is doped with an acceptor impurity,  $E_F$  shifts towards the valence band maximum. In this case, the formation energy of the charged donor-type defects decreases. With the valence band maximum being far from the vacuum level, the decrease in the formation energy of donor defects can be substantial [25] which favors their formation and also result in compensating the very acceptor impurities that one is attempting to incorporate. Let us consider in greater detail the

donor defects which known to be the major “killers” of *p*-type ZnO.

**O vacancies.**  $V_O$  is a deep donor in ZnO as predicted by theory and determined from EPR experiments [16] [26]. Therefore, it is not responsible for *n*-type conductivity. However, oxygen vacancies have a low formation energy in *p*-type ZnO [16], and therefore, they can compensate the intended acceptors.

**Zn interstitials.** Zn interstitials are shallow donors [27] [28]. They are probably responsible for the ~ 30-meV donor centers created by electron irradiation [17].  $Zn_i$  is reported to have a high formation energy in *n*-type material [29] but it reduces dramatically when the Fermi level approaches the valence band [25]. This means that it too could be responsible for thwarting efforts to achieve *p*-type conductivity.

**Zn anticites.** Zn anticites ( $Zn_O$ ) are deep donors. However, they have a large formation energy and thus unlikely to act as major compensation centers in *p*-type ZnO [25].

In addition to the fundamental problem of acceptor compensation by native defects, chemical elements acting as donors can also pose a problem in attaining *p*-type material since they can out-diffuse from the substrate or be incorporated in the growing ZnO film from the growth environment such sample holders, process gases, chamber walls, *etc.*, and the raw materials where they are present as impurities. The major donor impurities in ZnO are discussed below.

**Hydrogen:** Hydrogen is not amphoteric in ZnO and always acts as a donor [18]. The ionization energy of a hydrogen donor is ~ 35 – 40 meV [30] [31]. It is typically not the dominant donor in the as-grown bulk ZnO with the exception of the material fabricated by seeded chemical vapor transport where hydrogen contributes significantly to the conductivity [31]. However, hydrogen is omnipresent in metal-organic chemical vapor deposition (MOCVD) systems and is a fast diffuser even at a temperature of, *e.g.*, 600 °C [32] [33]. Hydrogen passivates acceptors, such as  $N_O$ , by forming H-A complexes. A signature of hydrogen’s presence in ZnO is the 3.363 eV donor-bound exciton line in photoluminescence spectra which is usually denoted as line  $I_4$  [34].

**Group III elements** (Al, Ga, In) on the Zn sites: Ionization energies of Al, Ga, and In donors are 53, 55, and 63 meV, respectively [34]. Group-III elements can out-diffuse from the foreign substrates, *e.g.*, Al from sapphire [35] [36] or Ga from GaN [34] on which the epitaxial layers are grown and could aggravate efforts to achieve *p*-type conductivity ZnO layers.

**Group-VII elements** (F, Cl, Br) on O-sites: Highly conductive *n*-type ZnO films doped with F [37] [38] and Cl [39] have been reported. The experimental data show that concentrations of intentional F and Cl donors in ZnO can be of the order of  $10^{20} \text{ cm}^{-3}$  pointing to high solubility limits. No data on the diffusivities of these elements and ionization energies of the corresponding donor centers are available at the present time.

In addition to the rather fundamental problem of doping asymmetry, inhomogeneous impurity incorporation causes potential fluctuations which defeat the purpose to some extent and also in turn make the determination of the conductivity type via the Hall effect rather difficult. Conducting substrates, such

as ZnO, GaN, Si, GaAs, heterogeneous systems, such as ZnO on GaN/Si and ZnO on GaN/sapphire, could provide parallel conduction channels, which could also occur via conduction (polarity)-type conversion. For example, if semi-insulating or *n*-type GaAs substrate is used, one should consider the possibility of its conversion to *p*-type conductivity due to Zn-diffusion. Grain boundaries, surface conduction [40], impurity segregation and even the formation of two-dimensional electron gas (2DEG) at the film/foreign substrate interfaces can be responsible for parallel conduction. Further complications can be introduced due to the fact that and microcrystalline material can show positive Hall coefficient.

To exemplify the effect of multilayer conduction let us discuss the well-known problem of Hall-effect analysis for a semiconductor with two-band conduction (co-existing *n*- and *p*-type regions) [41]. This has been discussed recently by Claflin *et al.* [42] in the context of ZnO. The Hall coefficient in a material with two-band conduction can be expressed as:

$$R_H = \frac{R_p \sigma_p^2 + R_n \sigma_n^2}{(\sigma_p + \sigma_n)^2} = \frac{p\mu_p^2 - n\mu_n^2}{e(p\mu_p + n\mu_n)^2} \quad (1)$$

It is clear that  $R_H \rightarrow 0$ , when  $p\mu_p^2 - n\mu_n^2 = 0$ , in which case a singularity occurs in the apparent carrier concentration if the single-band analysis of the Hall measurements is employed for samples with two-band conduction. Using typical values  $\mu_p = 1 \text{ cm}^2/\text{Vs}$ ,  $\mu_n = 200 \text{ cm}^2/\text{Vs}$ , and  $p = 4 \times 10^{18} \text{ cm}^{-3}$ , a transition from *p*-type ( $R_H > 0$ ) to *n*-type ( $R_H < 0$ ) polarity will be observed for electron concentrations in *n*-type channel as low as  $\sim 1 \times 10^{14} \text{ cm}^{-3}$ . The above treatment naturally assumes that the cyclotron motion within the sample is not hindered, except by the physical boundaries of the sample. When localization takes place, which is an endemic problem in wide bandgap semiconductors doped with acceptor-type impurities particularly at high concentrations, the carriers are trapped in a sense and cannot really follow the electric field induced force (for small values of field which is the case in Hall measurements) and Lorentz force. When and if this happens, the applicability of the conventional Hall measurements would come under question, particularly at low temperatures.

### III. CURRENT STATUS OF P-TYPE DOPING

Known acceptors in ZnO are *group IA* elements (Li, Na, K), *group IB* elements (Cu, Ag, Au), *group VA* elements (N, P, As, Sb), and Zn vacancies. Intrinsic *p*-doping via Zn-vacancies is not reliable, because it is difficult to control the needed small deviations from stoichiometry and stability of non-equilibrium point defects. Therefore, the main approach for achieving *p*-type ZnO is the substitution of some of the host matrix elements with acceptor impurities.

One possible approach is the introduction of a *group IA* element, such as Li, Na, and K on Zn sites. As predicted by the density functional theory (DFT) [43], Li, Na, and K form acceptor levels are at 0.09, 0.17, and 0.32 meV above the maximum of the valence band, respectively. Table 1 summarizes ionization energies for known acceptors, both predicted by theory and measured in experiments. However, doping with *group IA* elements suffers from their very high diffusivities as well as self-compensation by occupying

interstitial positions where they act as donors [44]. For instance, doping with lithium creates semi-insulating ZnO [45] because of additional interstitial Li atoms acting as donors [43] compensating the acceptors. Nevertheless, *p*-type ZnO layers with  $p \approx 1 \times 10^{17} \text{ cm}^{-3}$ ,  $\mu_p \approx 2.44 \text{ cm}^2/\text{Vs}$  have been reported using Li as an acceptor dopant [46]. Homojunction light-emitting diodes utilizing *p*-type ZnO doped with Na have also been reported recently [47] [48]. *P*-type layers showed hole concentration varying from  $4.85 \times 10^{17} \text{ cm}^{-3}$  to  $4.7 \times 10^{18} \text{ cm}^{-3}$  with low Hall mobilities ranging from 0.12 to 1.42  $\text{cm}^2/\text{Vs}$ , which are too low to accord confidence in the applicability of this particular measurement to these particular samples. Nevertheless, the ionization energy of Na acceptor was found to be 0.164 eV in agreement with the theoretical value of 0.17 eV [43].

As predicted by first-principle calculations [49], *group IB* elements, such as Cu, Ag, and Au, on Zn sites are acceptors with rather high ionization energies of 0.7, 0.4, and 0.5 eV, respectively, with much less tendency for self-compensation. It should be noted that the calculated ionization energy of  $\text{Cu}_{\text{Zn}}$  acceptors is in gross disagreement with the experimental data showing the value of  $\sim 3.2 \text{ eV}$  [50]. Several groups have recently reported *p*-type ZnO films doped with Ag [51] [52]. The reported values for free carrier concentration and mobility were  $p \leq 6 \times 10^{17} \text{ cm}^{-3}$  and  $\mu_p \leq 2.4 \text{ cm}^2/\text{Vs}$ .

In an effort to establish reliable *p*-type doping of ZnO, the majority of the attention has been paid to the *group VA* elements, mainly N, P, or As, which generate acceptor states if incorporated substitutionally on the oxygen sites. However, since their ionic radii are much larger than that of oxygen [1.38 Å for O, 1.68 Å for N (22% larger than that for O), 2.12 Å for  $\text{P}^{3-}$  (51% larger), 2.22 Å for  $\text{As}^{3-}$  (59% larger), and 2.45 Å for Sb (55% larger)], the density functional theory [43] suggests significantly deeper acceptor levels (0.40, 0.93, and 1.15 eV for N, P, and As, respectively), as compared to the *group IA* elements (see Table 1). Because of the large difference in atomic radius between O and  $\text{Sb}^{3-}$ , the binding energy of this impurity has not been calculated accurately, but presumed to be the relatively high. It is believed that the best candidate for *p*-type doping in ZnO is N, because it has the smallest ionic radius (1.68 Å) among the *group-V* impurities mentioned above [43]. Despite only 22% larger ionic radius, N was found to create a rather deep acceptor level of  $\sim 0.165 \text{ eV}$  [53] [54] (note that the experimental value is lower than the predicted value of 0.4 eV [43]). Furthermore, its incorporation on the lattice sites is insufficient to produce high hole concentrations [22]. Another unattractive feature of nitrogen is that it has the tendency to self-compensate via the formation of molecular  $\text{N}_2$  centers on O sites which are donors [55] [56]. Consistently, many groups reported weak *p*-type conduction with hole concentration in the mid- $10^{17} \text{ cm}^{-3}$  range and  $\mu_p \approx 1\text{-}2 \text{ cm}^2/\text{Vs}$  [57]-[59] for N doping. The improvement of epitaxial technology and doping techniques resulted in enhanced mobilities of 8  $\text{cm}^2/\text{Vs}$  and 25  $\text{cm}^2/\text{Vs}$  reported for very high quality epitaxial films grown by laser molecular beam epitaxy (MBE) [60] and radical-source MBE [61], respectively. However, the measured hole concentrations are still moderate ( $< 5 \times 10^{17} \text{ cm}^{-3}$ ) which is insufficient for applications in light-emitting devices.

TABLE 1. CALCULATED AND EXPERIMENTAL VALUES OF IONIZATION ENERGIES,  $E_i$ , FOR SUBSTITUTIONAL ACCEPTORS IN ZnO AND CALCULATED IONIZATION ENERGIES,  $E_{def}$ , FOR PROPOSED ACCEPTOR DEFECT CENTERS INVOLVING GROUP VA ELEMENTS.

Group	Element	Ionic radius (Å)	$E_i$ (eV)		Proposed acceptor center	$E_{def}$ (eV)
			Theory	Experiment		
Group IA	Li	2.03	0.09 Ref. [44]			
	Na	2.1	0.17 Ref. [44]	0.164 Ref. [48]		
	K	2.42	0.32 Ref. [44]			
Group IB	Cu	-	0.7 Ref. [50]	3.2 Ref. [51]		
	Ag	-	0.4 Ref. [50]			
	Au	-	0.5 Ref. [50]			
Group VA	N	1.68	0.40 Ref. [44]	0.165 Ref. [54]		
	P	2.12	0.93 Ref. [44]	0.18 Ref. [90]	$P_{Zn}-2V_{Zn}$	0.18 Ref. [88]
	As	2.22	1.15 Ref. [44]	0.12 Ref. [89]	$As_{Zn}-2V_{Zn}$	0.15 Ref. [87]
	Sb	2.45	-	0.14 Ref. [83]	$Sb_{Zn}-2V_{Zn}$	0.16 Ref. [87]

It has been shown theoretically [20] that co-doping with acceptor (N) and donor (Al, Ga, or In) impurities in the 2:1 ratio in ZnO can stabilize substitution of N at the appropriate O lattice site through the formation of N-Ga-N (acceptor-donor-acceptor or ADA for short) bonds, similar to co-doping experiments in GaN using Mg and O. Wang and Zunger [62] proposed so-called cluster doping, *i.e.*, doping with even more partner atoms than in co-doping, to further promote acceptor formation. However, it should be realized that the isolated Ga atoms can compensate the N-Ga-N acceptors [63] reducing the efficacy of this approach. Numerous experimental studies based on the co-doping approach have revealed discrepancies between the theory and experiments and resulted in little or no success in terms of achieving stable *p*-type material with reasonably high free-hole mobility. The reported mobilities typically do not exceed 1-2 cm<sup>2</sup>/(Vs) [21] [22] [64]-[67].

Other *group V* elements for substitutional doping on the O sites, including P [68]-[74], As [75]-[79], and even Sb [80]-[82], have received relatively less attention as compared to N. Despite the fact that ionic radii of these dopants far exceed that of oxygen, *p*-type conductivity has been reported for ZnO doped with P [71], As [76], and Sb, [81] [82], with  $p > 10^{18}$  cm<sup>-3</sup> and  $\mu_p = 20$  cm<sup>2</sup>/(V s) in ZnO:Sb [81] and  $\mu_p = 11$  cm<sup>2</sup>/(V s) in ZnO:As [76]. Weak *p*-type conductivity with  $p = 2.7 \times 10^{16}$  cm<sup>-3</sup> and  $\mu_p = 8.2$  cm<sup>2</sup>/(V s) has also been reported for P-doped ZnMgO grown by PLD [83]-[85]. To explain these somewhat perplexing findings, Limpijumnong *et al.* [86] proposed a model for large-size-mismatched *group-V* dopants in ZnO implemented with first-principles calculations. The model is based on the premise that dopant atoms do not occupy O sites as is widely perceived, but rather Zn sites, each forming an  $A_{zn}-2V_{zn}$  ( $A = P, As, Sb$ ) complex with two spontaneously induced Zn vacancies in a process that involves a five-fold coordination of a dopant atom. Calculations [86] indicate that the  $As_{zn}-2V_{zn}$  defect complex should give rise to an acceptor level at about 0.15 eV above the valence band maximum, shallower than that of  $As_O$ , and lower than formation energy than any of the parent defects ( $As_{zn}$  and  $V_{zn}$ ). When applied for Sb and P, the same scenario results in predicted ionization energies of 0.16 and 0.18 eV for  $Sb_{zn}-2V_{zn}$  [86] and  $P_{zn}-2V_{zn}$  [87] centers, respectively. As seen from Table 1, the ionization energies calculated for the  $A_{zn}-2V_{zn}$  complexes are in

reasonable agreement with acceptor ionization energies found experimentally for ZnO doped with Sb (0.14 eV [82]), As (0.12 eV [88]), and P (0.18 eV [89]) and much lower than those predicted for  $As_O$  [43] and presumed for  $Sb_O$  [86] acceptors. Therefore, these data suggest the formation of  $A_{zn}-2V_{zn}$  defect-impurity complexes are responsible for the acceptor levels in ZnO doped with As, P, and Sb. The implicit assumption here of course is that the experimental values are dependable. As we pointed out, in systems with substantial localization, which is very likely to be the case here, the application of Hall measurements should be with extreme care. Further, when applied, the previous state of the system, temperature, and also evolved time would lead to deviations in results. From the viewpoint of device applications, stability of these centers is very important, because heat treatments during device fabrication or elevated temperature device operation in the high injection current and electric field regime can result in different data or complex decomposition leading to conduction-type (polarity) inversion. For instance, a fast decay of emission efficiency (within few hours) during device operation has been reported for light-emitting structures with *p*-type regions doped with nitrogen [90] and phosphorous [91]. Although light-emitting diodes and even lasing have been reported for ZnO-based structures with *p*-type layers doped both with As [92] [93] and Sb [94] [95], the data on the stability of acceptor centers in ZnO doped with As and Sb are unavailable at present time.

A new insight into the *p*-type problem has been provided by recent studies of local conductivity in acceptor-doped ZnO grown by the MOCVD [96]-[98] and spray pyrolysis [99] methods using scanning capacitance microscopy (SCM) and scanning surface potential microscopy (SSPM), which are variants of atomic force microscopy (AFM). It has been demonstrated that impurities are preferentially incorporated at or near growth defects [96]. Depending on the growth parameters, extended *p*-type domains surrounded by *n*-type regions were observed. Clearly this represents an extreme case of localization both in the conduction and valence bands. The local conductivity type has been directly correlated with the topography in that smooth two-dimensional surfaces exhibit *p*-type conductivity whereas the *n*-type conductivity is seen in regions with three-dimensional island growth or structural defects, such as microcracks or surface pits. Fig. 2 shows a



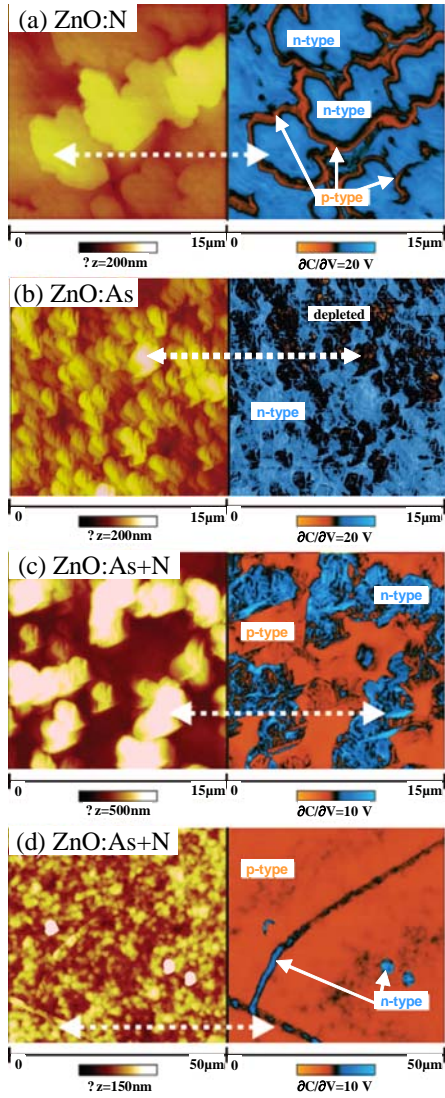


Fig. 2. Typical AFM (left) and SCM(right) images of MOCVD ZnO layers doped with (a) nitrogen and (b) arsenic and (c) and (d) co-doped with both acceptor species, but with different surface morphologies. The surfaces of the mono-doped samples exhibit three-dimensional islands with typical diameters of about 5–8 and 1–2 μm for N and As doping, respectively (a) and (b). The corresponding SCM images show dominant *n*-type regions despite the acceptor doping. Very small *p*-type domains (depicted by arrows) exclusively related to island/grain boundaries were found only for ZnO:N (a), whereas ZnO:As revealed no significant *p*-type regions, but a majority of depleted areas (dark) due to the smaller grains and the superimposed space-charge regions (b). For the dual-doped layers, image (c) shows a typical sample with mixed conductivity, *i.e.*, with dominant three-dimensional islands which are of *n*-type in SCM and with smoother, *p*-type regions. In contrast, the sample grown under conditions yielding very flat surface (d) reveals dominant smooth *p*-type domains which are only partly disturbed by very few microcracks and three-dimensional islands which are all *n*-type (depicted by arrows) (courtesy of A. Krost).

mosaic of AFM and SSPM images for ZnO layers grown by metal-organic chemical vapor deposition (MOCVD). For the films co-doped with As and N, stable *p*-type ZnO was achieved if the growth was two dimensional and yielded smooth surfaces (see Fig. 2). In contrast, the acceptor doping completely failed if the growth was three-dimensional [96] [97]. These data show again that a fundamental understanding of impurity-defect interaction is of vital importance for the control over the

conductivity type in ZnO. Another clear message is that the density of extended defects (grain boundaries and very likely dislocations and stacking faults) should be minimized for successful *p*-type doping. These observations appear to indicate that successful *p*-doping can be achieved by growing homoepitaxial ZnO films on high-quality ZnO substrates which are becoming commercially available now. The two-dimensional growth mode easily attainable for homoepitaxy would obviously have the added benefit of reducing the point-defect density. It should be noted that the majority of reported studies devoted to *p*-type doping of ZnO have been performed on heteroepitaxial film grown on foreign substrates, in most cases in 3-dimensional growth mode. This is part due to the unavailability of native substrates until recently.

#### IV. STRATEGIES USED TO POTENTIALLY OVERCOME P-TYPE PROBLEM

After more than a 10-year quest for a robust and stable *p*-type ZnO, it became clear that the straightforward approaches did not lead to any major breakthrough in achieving competitive ZnO *p-n* junctions suitable for light-emitting devices. Another approach for tackling the *p*-type problem is, therefore, warranted. In this section we will consider several approaches proposed recently by Wei and co-workers [24] [49] [55] [86], which are based on first-principles calculations of the defect formation energies and transition energies of intrinsic and extrinsic defects. It was suggested that (i) the solubility of acceptor impurities can be increased by adjusting their chemical potential using non-equilibrium growth methods (MBE, MOCVD, *etc.*); (ii) the ionization energy of acceptor levels can be reduced by designing shallower dopants or dopant complexes; (iii) both the ionization energy of acceptor level and defect compensation can be reduced by modifying the host band structure near the band edges.

##### A. Improving dopant solubility

The solubility limit for acceptor impurities in ZnO, as well as other wide-gap materials suffering from doping asymmetry, can be enhanced above the thermodynamic limit by employing “non-equilibrium” growth techniques, such as MBE and MOCVD. One way to improve the dopant solubility is through adjusting dopant chemical potential  $\mu_A$ . The chemical potential of an acceptor dopant in the ZnO matrix determines the dopant solubility. Therefore, raising this potential would increase the solubility of the dopant coupled with avoidance of precipitate formation [100].

Fig. 3 shows the calculated formation energies of charge neutral defects as a function of the O chemical potential. Here, the chemical potential of nitrogen,  $\mu_N$ , is derived from  $N_2$  gas. It is seen from the figure that the formation energy of nitrogen acceptors on oxygen sites,  $N_O$ , is lower under the O-poor conditions, but higher when the conditions are O-rich. It should be noted that O-poor or O-rich conditions can be controlled during growth through the flux of oxygen radicals arriving at the substrate surface in radical-source MBE or through the ratio of Zn- and O-containing precursors in MOCVD. The vertical dashed line in the figure separates the regions where  $N_3N_2$  will (region to the left of the line) and will not precipitate (region to the right of the line) under the

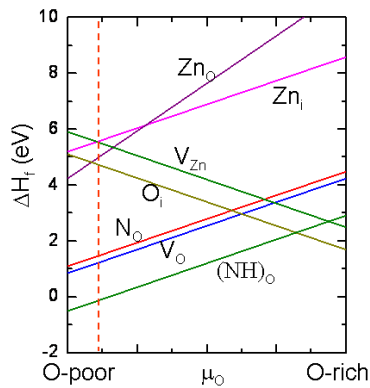


Fig. 1. Formation energies,  $\Delta H_f$ , for intrinsic defects and  $(\text{NH})_O$  in ZnO calculated by using first-principles density-functional theory (courtesy of Y. F. Yan and S. H. Wei).

thermodynamically equilibrium growth conditions. These calculations show that the precipitation of a secondary phase can limit the solubility of dopants. If non-equilibrium growth techniques is used, the precipitation can be suppressed, *e.g.*, by growing ZnO at low temperatures. However, in this case, the acceptors often need to be activated by heat treatment at temperature higher than the growth temperature. Therefore, the  $\text{Zn}_3\text{N}_2$  phase may appear upon annealing. As seen in Fig. 3, to enhance the solubility of nitrogen, ZnO films should be synthesized under the O-poor conditions. However, the formation energies for “acceptor-killer” defects, such as  $\text{Zn}_i$  and  $\text{V}_O$ , also decrease under the O-poor conditions, making them more likely. Thus, there is an inherent conflict in our attempts for enhancing the *p*-type doping if  $\text{N}_2$  is used as a dopant. From a practical point of view, some additional obstacles may arise on the growth side. One known problem is the strong relationship between the growth mode and growth conditions for non-equilibrium growth techniques. For instance, high quality Zn-polar ZnO can be grown by MBE only under oxygen rich conditions. The reduction of the O/Zn ratio results in three-dimensional material with very rough surface morphology [101] which is a very undesirable scenario because, as mentioned above, impurities are preferentially incorporated at or near growth defects [96] [97]. MBE growth of high-quality O-polar ZnO calls for roughly a 1:1 O/Zn ratio, and any deviation towards either O-poor or O-rich conditions shifts the tendency of growth towards 3-dimensional (3D) mode and thus deteriorates the material quality [102]. One should note that while the theory deals with the thermodynamically equilibrium point defects, non-equilibrium defects also should be considered. Atomically smooth surfaces synonymous with 2D growth prevents the generation of both extended and non-equilibrium point defects, while the 3D growth mode strongly favors their formation. We should be aware, however, that adding dopant species to the system can shift the optimum growth window. What is clear is that this problem needs further theoretical and experimental attention.

To resolve the dilemma, how to increase the solubility of a desired dopant and to prevent at the same time formation of compensating defects, two different approaches have been proposed: (i) tuning the Fermi energy of ZnO; (ii) selecting appropriate dopant precursors.

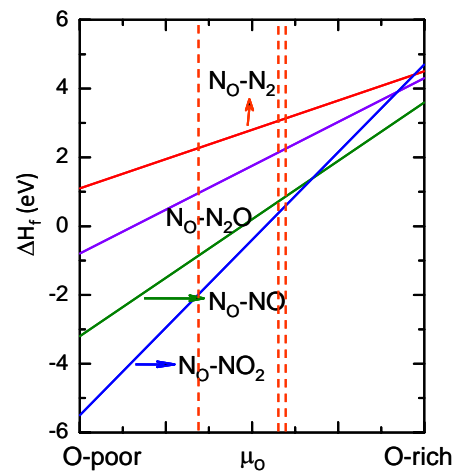


Fig. 4. Calculated formation energies of neutral  $\text{N}_O$  centers for different nitrogen precursors as functions of the O chemical potential. The left, middle, and right dashed vertical lines indicate the limits for O chemical potentials below which  $\text{Zn}_3\text{N}_2$  will precipitate for  $\text{N}_2\text{O}$ , NO, and  $\text{NO}_2$  molecules, respectively (courtesy of Y. F. Yan and S. H. Wei).

The solubility of both the dopants and compensating defects depends critically on the Fermi level. If we could pin the Fermi level at a desired position, then we may enhance the solubility of a dopant and suppress the formation of compensating defects. One popular approach to control the Fermi level position is passivating the dopants by hydrogen. Hydrogen passivation is well known in a plethora of semiconductor systems, such as various III-V systems [103] [104], non-oxide II-VI semiconductors, [105] [106], and III-nitrides [107] [108]. For example, in Mg-doped GaN, introduction of H can prevent the Fermi-level from shifting, passivates Mg, and increases the solubility of Mg as well [107]. After the growth, H is driven out by annealing in an H void environment to achieve *p*-type conductivity. Likewise, in addition to preventing the Fermi level shift, co-doping with H can directly passivate N dopants by forming molecular NH complexes on O sites  $[(\text{NH})_O]$  in ZnO:N. The binding energy for  $(\text{NH})_O$  is 2.9 eV and  $(\text{NH})_O$  complexes electronically mimic the O atoms (*i.e.*, act neither as donors nor acceptors) and cause a smaller lattice distortion than  $\text{N}_O$ . Thus, the concentration of  $(\text{NH})_O$  in ZnO can be made much higher than that of  $\text{N}_O$  [109]. As seen from

As seen from Fig. 3, the calculated formation energy of  $(\text{NH})_O$  is much lower than the formation energies of  $\text{N}_O$  and the major compensating defects ( $\text{O}_V$  and  $\text{Zn}_i$ ) under the O-poor conditions. As elucidated above, *p*-type dopants are activated by driving out the hydrogen atoms from the sample during post-growth thermal annealing. Several studies have reported hydrogen-assisted N-doping of ZnO [110] [111]. To date, the reported carrier concentrations and mobilities do not yet exceed values reported by employing other approaches ( $p < 1 \times 10^{18} \text{ cm}^{-3}$ ,  $\mu_p \leq 1 \text{ cm}^2/\text{Vs}$ ), if indeed the reported values are reliable (note very low mobility value pointing to the strong localization in this material).

Solubility of nitrogen acceptors in ZnO can also be enhanced by metastable molecular doping. There are at least four different gases, namely  $\text{N}_2$ , NO,  $\text{NO}_2$ , and  $\text{N}_2\text{O}$ , that can be used as nitrogen dopant source [55] [112]. If these molecules

arrive intact at the growing surface, their chemical potentials will determine the doping efficiency. Fig. 4 shows the calculated formation energies of  $N_O$  neutral centers for 4 different nitrogen precursors ( $N_2$ ,  $N_2O$ ,  $NO$ ,  $NO_2$ ) as a function of oxygen chemical potential. As seen from the figure, the nitrogen solubility can be enhanced significantly, if metastable  $NO$  or  $NO_2$  gases are used as the nitrogen source. The reason why doping with  $NO$  or  $NO_2$  should result in higher solubility of nitrogen as compared to  $N_2$  and  $N_2O$  is that these molecules can supply nitrogen atoms by breaking only the weak N–O bonds, whereas the strong N–N bonds need to be broken in the cases of  $N_2$  and  $N_2O$  nitrogen precursors. One should note that molecular doping is already employed in gas-phase growth techniques such as MOCVD, but have not given rise to any major improvement of  $p$ -type doping. Similarly, in radical-source MBE plasma sources are already employed for cracking gas molecules which allow dopant species to arrive on the growing surface in a form of very reactive radicals. Therefore, the molecular gas dopant source approach is unlikely to improve nitrogen incorporation in radical source MBE. The molecular doping mainly using  $NO$  as a nitrogen precursor have been employed in many experimental studies (*e.g.*, see [113] [114]). However, the reliable  $p$ -type material with free-carrier concentrations well in excess of  $10^{17} \text{ cm}^{-3}$  has not been reported yet to the best of our knowledge.

#### B. On designing shallow acceptor levels in ZnO

Since the valence bands of most compound semiconductors are formed mainly by the orbitals associated with anion atoms, acceptor dopants on cation sites generally cause smaller perturbation of the valence band than dopants on the anion sites. As the results, dopants on cation sites produce shallower acceptor levels than dopants on anion sites [24] [49]. An additional benefit of the acceptor substitution on cation sites is that the self-compensation by anion vacancy ( $V_O$ ) also reduces. As discussed in Section III, *group I* elements on Zn sites are acceptors. However, *group IA* acceptors (Li, Na, K), despite shallow acceptor levels (see Table 1), suffer from self-compensation and are fast diffusers. *Group IB* elements are also unlikely to be very promising acceptors in ZnO, although the calculations by Yan *et al.* [49] have shown that the formation energies of *group IB* acceptors on Zn sites ( $Cu_{Zn}$ ,  $Ag_{Zn}$ ,  $Au_{Zn}$ ) are small under O-rich conditions, and the formation of donor defects is suppressed. The ionization energies of acceptor defects are too high (0.4 eV for  $Ag_{Zn}$  is the lowest among them) from a practical point of view. Therefore, *group I* acceptors do not seem very promising for achieving  $p$ -type ZnO.

Co-doping of ZnO with acceptors and isovalent atoms is another proposed approach [115] to lower the acceptor ionization energy. Using first-principles band-structure calculations, it was shown that the acceptor transition energies of  $V_{Zn}-O_O$  can be reduced by substituting O with more electronegative F to lower the electronic potential, whereas the transition energy of  $N_O$  acceptors can be reduced by replacing Zn with isovalent Mg or Be. In the latter case, the high ionization energy of  $N_O$  acceptors has its genesis in the strong coupling between the acceptor level and Zn 3*d*-orbitals. If we

replace the neighboring Zn atom by the isovalent Mg or Be atoms that have similar atomic sizes as Zn but with no occupied *d*-orbitals, the electron transition energy level of  $N_O + nMg_{Zn}$  (or  $nBe_{Zn}$ ) would be expected to be lower than that of  $N_O$  in

TABLE 2. CALCULATED BINDING ENERGY  $E_b$  OF THE ACCEPTOR DEFECT COMPLEX IN ZnO AND THEIR ELECTRON TRANSITION ENERGY BETWEEN THE NEUTRAL,  $E_{0/-}$ , AND FIRST IONIZED STATES AND ELECTRON TRANSITION BETWEEN THE FIRST AND SECOND IONIZED STATES,  $E_{-/2-}$  [115].

Defect	$E_b$ , (eV)	$E_{0/-}$ (eV)	$E_{-/2-}$ (eV)
$N_O$		0.31	
$N_O-Mg_{Zn}$	0.3	0.29	
$N_O-4Mg_{Zn}$	1.6	0.23	
$n$			
$N_O-Be_{Zn}$	0.1	0.22	
$N_O-4Be_{Zn}$	1.9	0.12	
$V_{Zn}$		0.18	0.34
$V_{Zn}-F_O$	-2.3	0.16	

ZnO. The largest reduction of the acceptor ionization energy is expected for  $n = 4$ , when the tetrahedral environment around  $N_O$  is preserved and no level splitting occurs. Table 2 summarizes the results of the first principles calculations for several proposed defect complexes [115].

As seen from Table 2, the  $N_O + nBe_{Zn}$  complexes have the lowest calculated ionization energy for single ionized acceptor (electron transition energy  $E_{0/-}$  between the neutral and first ionized states in **Error! Reference source not found.**). Therefore, Be could be a good co-dopant pair for nitrogen to achieve  $p$ -type ZnO. In the case of intrinsic  $p$ -doping via Zn-vacancies, co-doping with fluorine should lower the ionization energy of  $V_{Zn}$  acceptors [115]. However, the implementation of this approach may not be as straightforward as it seems at a first glance, because the isovalent co-doping of ZnO will result also in an increase of the band gap which usually gives rise to an increase of the ionization energies of donors and acceptors. Therefore, the doping profiles of acceptor and isovalent impurities should be carefully designed. Probably,  $\delta$ -doping with isovalent atoms can be applied to lower the acceptor ionization energy.

As discussed in Section III, doping with large atomic size *group VA* elements, such as P, As, and Sb, may also result in shallow defect levels. For instance, the atomic sizes of As and Zn are similar.  $As_{Zn}$  has a relatively low formation energy but it is a (triple) donor.  $V_{Zn}$  is a native (double) acceptor with low formation energy. However, one  $As_{Zn}$  and two  $V_{Zn}$  could bind strongly and form a new acceptor complex ( $As_{Zn}-2V_{Zn}$ ). This complex has a low formation energy, and its ionization energy is calculated to be  $\sim 0.15$  eV [86] which is in reasonable agreement with the measured value of 0.12 eV [88].



### C. Modification of the host band structure to reduce ionization energy and compensation

Another approach that has been proposed to reduce native-defect compensation and acceptor ionization energy is the modification of the host band structure by introducing a fully compensated impurity band near the valence band maximum of the host [116]. In theory this is accomplished by introducing a fully compensated defect band near the valence band maximum or the conduction band minimum through doping by mutually passivated donor-acceptor pairs. It should be noted that the concentration of the defects inducing the impurity band should exceed a certain percolation limit. Second, after the fully compensated insulating band is formed, excess acceptor dopants can be used in the passivated system to achieve *p*-type conductivity.

For instance, the valence band edge of ZnO can be modified by passivating co-dopants such as Ga and N. N combined with Ga creates a passivated defect band above the valence band maximum. Then, shallow acceptor levels can be created by doping the passivated ZnO:(Ga+N) system with excessive N. The calculated defect level of N in this scenario is located about 0.1 – 0.2 eV above the defect band. However, one should keep in mind that the introduction of such a defect band will result in dramatic degradation of electronic and optical properties of the material due to large lattice disorder. Strong carrier localization and, therefore, low hole mobility can be expected in a material with impurity-band doping. From a practical point of view, use such a material for carrier injection requires very high hole concentration, probably of the order of  $10^{20} \text{ cm}^{-3}$ .

### V. CONCLUSIONS

In conclusion, despite great strides and tantalizing data, a compelling argument can be made that no credible *p*-type ZnO suitable for light-emitting devices has been reported up to this point. Although *p*-type conductivity has been noted in ZnO doped with variety of impurities (virtually with all that have been tried), none of the approaches provided a reliable conduit for resolving the *p*-type problem and achieving robust LEDs. The defective nature of ZnO, localization induced by the candidate *p*-type impurities, and possibly other complications such as shunting conduction layers, *etc.*, make it very difficult to interpret the Hall-effect measurements. Report of a credible injection structure would lessen the emphasis on questions surrounding the Hall measurements. Several issues must be addressed for a successful resolution of the *p*-type problem in ZnO. Further reduction of point and extended defects which act as either compensating centers for the intended *p*-type impurities (point defects) or regions of localization for such centers (extended defects) is needed. Moreover, extended defects promote the formation of non-equilibrium point defects as well. Reduction in the unwanted impurities, many of which act as shallow or deep donors, compensating the acceptor impurities by proper designing of growth conditions is also necessary. Insight into the nature of acceptor centers in ZnO that will allow the prediction of their behavior, thermal stability, and elaboration on techniques for improving *p*-type impurity incorporation and activation are warranted.

The most straightforward avenue for addressing defects is by employing homoepitaxy on bulk ZnO substrates, which are available now, and by optimizing the growth conditions in such a way that the formation energies for compensating donors would increase. Additionally homoepitaxy promotes two-dimensional growth mode which in turn suppresses the formation of extended and non-equilibrium point defects. The unwanted impurity concentration can be addressed by improving growth techniques in regard to both thin films and bulk material. Development of theoretical models predicting defect and impurity-defect centers in ZnO and combination of modern analysis techniques, such as x-ray extended absorption fine structure or Z-contrast scanning transmission electron microscopy together with energy dispersive spectroscopy and electron-energy loss spectroscopy would provide insight into the nature of these centers and establish control over the electrical properties of ZnO. All these together would have the potential to pave the way for “useful” *p*-type ZnO.

### ACKNOWLEDGEMENT

We thanks Dr. J.F. Yan and Dr. S.H. Wei (National Renewable Energy Laboratory, Golden, CO USA) for providing the original results of their first-principle calculation of defect formation energies in ZnO and Prof. A. Krost (Institute of Experimental Physics, Otto Von Guericke University of Magdeburg, Magdeburg, Germany) for AFM and SCM images. This work is sponsored by Air Force Office of Scientific Research.

### REFERENCE

- [1] Ü. Özgür, Y.I. Alivov, C. Liu, A. Teke, M.A. Reshchikov, S. Dogan, V. Avrutin, S.J. Cho, and H. Morkoç, “A comprehensive review of ZnO materials and devices”, *J. Appl. Phys.*, vol. 98, no. 4, pp. 041301-1-103, Aug.2005.
- [2] C. Klingshirn, “ZnO: from basics towards applications”, *Phys. Stat. Sol. (b)*, vol. 244 no. 9, pp. 3027-3073, Sep. 2007.
- [3] Ü. Özgür, D. Hofstetter, and H. Morkoç, “ZnO Devices and Applications: A review of current status and future prospects”, *this issue*.
- [4] J. Fan and R. Freer, “The roles played by Ag and Al dopants in controlling the electrical-properties of ZnO varistors”, *J. Appl. Phys.*, vol. 77, no. 9, pp. 4795-4800, May 1995.
- [5] W.F. Shen, Y. Zhao, and C.B. Zhang, “The preparation of ZnO based gas-sensing thin films by ink-jet printing method”, *Thin Solid Films*, vol. 483, no. 1-2, pp. 382-387, Jul. 2005.
- [6] J. Suehiro, N. Nakagawa, S.-I. Hidaka, M. Ueda, K. Imasa, M. Higashihata, T. Okada, and M. Hara, “Dielectrophoretic fabrication and characterization of a ZnO nanowire-based UV photosensor”, *Nanotechnology*, vol. 17, no. 10, pp. 2567-2573, May 2006.
- [7] A. Ohtomo, S. Takagi, K. Tamura, T. Makino, Y. Segawa, H. Koinuma, and M. Kawasaki, “Photo-irresponsive thin-film transistor with Mg<sub>x</sub>Zn<sub>1-x</sub>O channel”, *Jpn. J. Appl. Phys.*, vol. 45, no. 24-28, pp. L694-696, Jul. 2006.
- [8] Y.J. Li, Y.W. Kwon, M. Jones, Y.W. Heo, J. Zhou, S.C. Luo, P.H. Holloway, E. Douglas, D.P. Norton, Z. Park, and S. Li, “Progress in semiconducting oxide-based thin-film transistors for displays”, *Semicond. Sci. Technol.*, vol. 20, no. 8, pp. 720-725, Aug. 2005.
- [9] R.L. Hoffman, B. J. Norris, and J. F. Wager, “ZnO-based transparent thin-film transistors”, *Appl. Phys. Lett.*, vol. 82, no. 5, pp. 733-735, Feb. 2003.
- [10] B.-Y. Oh, M.-C. Jeong, T.-H. Moon, W. Lee, J.-M. Myoung, J.-Y. Hwang, and D.-S. Seo, “Transparent conductive Al-doped ZnO films for

- liquid crystal displays", J. Appl. Phys., vol. 99, no. 12, pp. 124505-1-3, Jun. 15 2006.
- [11] C.G. Granqvist, "Transparent conductors as solar energy materials: A panoramic review", Sol. Energy Mater. Sol. Cells, vol. 91, no.17, pp. 1529-1598, Oct. 2007.
  - [12] S. B. Zhang, S.-H. Wei, and A. Zunger, "A phenomenological model for systematization and prediction of doping limits in II-VI and I-III-VI<sub>2</sub> compounds", J. Appl. Phys., vol. 83, no. 6, pp. 3192-3196, Mar. 1998.
  - [13] S. B. Zhang, S.-H. Wei, and A. Zunger; "Overcoming doping bottlenecks in semiconductors and wide-gap materials", Physica B, vol. 273-274, no. 12, pp. 976-980, Dec. 1999.
  - [14] D.C. Look, "Donors and Acceptors in Bulk ZnO Grown by the Hydrothermal, Vapor-Phase, and Melt Processes", MRS Symposia Proceedings Vol. 957 (Materials Research Society, Pittsburgh, 2007), p. 127. pp. 0957-K08-05-1-7.
  - [15] W. Walukiewicz, "Defect formation and diffusion in heavily doped semiconductors", Phys. Rev. B., vol. 50, no. 8, pp. 5221-5225, Aug. 1994.
  - [16] A. Janotti and C.G. Van de Walle, "Oxygen vacancies in ZnO", Appl. Phys. Lett., vol. 87, no. 12, pp.122102-1-3, Sep. 2005.
  - [17] D. C. Look, J. W. Hemsky, and J. R. Sizelove, "Residual Native Shallow Donor in ZnO", Phys. Rev. Lett., vol. 82, no. 12 pp. 2552-2555, Mar. 1999.
  - [18] C.G. Van de Walle, "Hydrogen as a Cause of Doping in Zinc Oxide", Phys. Rev. Lett., vol. 85, no. 5, pp. 1012-1015, Jul. 2000.
  - [19] F. Tuomisto, V. Ranki, K. Saarinen, and D.C. Look; "Evidence of the Zn Vacancy Acting as the Dominant Acceptor in n-Type ZnO", Phys. Rev. B.; **91**, 205502, (2003), vol. 91, no. 20, pp. 205502-1-4, Nov. 2003.
  - [20] T. Yamamoto and H. Katayama-Yoshida, "Solution using a codoping method to unipolarity for the fabrication of p-type ZnO", Jpn. J. Appl. Phys., Part 2, vol. 38, no. 2B, pp. L166-L169, Feb. 15 1999.
  - [21] K. Nakahara, H. Takasu, P. Fons, A. Yamada, K. Iwata, K. Matsubara, R. Hunger, and S. Niki, "Interactions between gallium and nitrogen dopants in ZnO films grown by radical-source molecular-beam epitaxy", Appl. Phys. Lett., vol. 79, no. 25, pp. 4139-4141, Dec. 2001.
  - [22] S.J. Pearton, D.P. Norton, K. Ip, Y.W. Heo, and T. Steiner; "Recent advances in processing of ZnO", J. Vac. Sci. Technol. B, vol. 22, no. 3, pp. 932-948, May-Jun. 2004.
  - [23] T. M. Barnes, K. Olson, and C.A. Wolden, "On the formation and stability of p-type conductivity in nitrogen-doped zinc oxide", Appl. Phys. Lett., vol. 86, no. 11, pp. 112112-1-3, Mar. 2005.
  - [24] Y.F. Yan and S.H. Wei, "Doping asymmetry in wide-bandgap semiconductors: Origins and solutions," Phys. Stat. Sol. (b), vol. 245, vol. 4, pp. 641-652, Apr. 2008.
  - [25] A. Janotti and C.G. Van de Walle, "Native point defects in ZnO", Phys. Rev. B, vol. 76, no. 16, pp. 165202-1-22, Oct. 2007.
  - [26] K. Vanheusden, C.H. Seager, W.L. Warren, D.R. Tallant, and J.A. Voight, "Correlation between photoluminescence and oxygen vacancies in ZnO phosphors", Appl. Phys. Lett., vol. 68, no. 3, pp. 403-405, Jan. 1996.
  - [27] F. Oba, S.R. Nishitani, S. Isotani, H. Adachi, and I. Tanaka, "Energetics of native defects in ZnO", J. Appl. Phys., vol. 90, no. 7, pp. 824-828, Jul. 2001.
  - [28] S. B. Zhang, S.-H. Wei, and A. Zunger, "Intrinsic n-type versus p-type doping asymmetry and the defect physics of ZnO", Phys. Rev. B, vol. 63, no. 7, pp. 075205-1-7, Feb. 2001.
  - [29] A. F. Kohan, G. Ceder, D. Morgan, and Chris G. Van de Walle, "First-principles study of native point defects in ZnO", Phys. Rev. B, vol. **61**, No.no., pp. 15019-15027, 2000.
  - [30] S.F.J. Cox, E.A. Davis, S.P. Cottrell, P.J. C. King, J.S. Lord, J.M. Gil, H.V. Alberto, R.C. Vilão, J. Pirotto Duarte, N. Ayres de Campos, A. Weidinger, R. L. Lichti, and S. J. C. Irvine, "Experimental Confirmation of the Predicted Shallow Donor Hydrogen State in Zinc Oxide", Phys. Rev. Lett., vol. 86, no. 12, pp. 2601-2604, Mar. 2001.
  - [31] D.M. Hofmann,, A. Hofstaetter, F. Leiter, H. Zhou, F. Henecker, B.K. Meyer, S.B. Orlinskii, J. Schmidt, and P.G. Baranov,, "Hydrogen: a relevant shallow donor in zinc oxide", Phys. Rev. Lett., vol. **88**, no., pp. 045504-1 - 045504-4, Jan. 2002.
  - [32] D.C. Look, R.L. Jones, J.R. Sizelove, N.Y. Garces, N.C. Giles, and L.E. Halliburton, "The path to ZnO devices: donor and acceptor dynamics", Phys. Stat. Sol. (a), vol. 195, no. 1, pp. 171-177, Jan. 2003.
  - [33] K. Ip, M.E. Overberg, Y.W. Heo, D.P. Norton, S.J. Pearton, C.E. Stutz, B. Luo, F. Ren, D.C. Look, and J.M. Zavada, "Hydrogen incorporation and diffusivity in plasma-exposed bulk ZnO", Appl. Phys. Lett., vol. 82, no. 3, pp. 385-387, Jan. 2003
  - [34] B. K. Meyer, H. Alves, D. M. Hofmann, W. Kriegseis, D. Forster, F. Bertram, J. Christen, A. Hoffmann, M. Straßburg, M. Dworak, U. Haboeck, and A. V. Rodina, "Bound exciton and donor-acceptor pair recombinations in ZnO", Phys. Stat. Sol. (b), vol. 241, no. 2, pp. 231-260, Feb. 2004.
  - [35] A. Dadgar, A. Krtischil, A. Diez, F. Bertram, J. Bläsing, J. Christen, A. Krost, in Third International Conference on Materials for Advanced Technologies, Singapore 2005, paper N-6-OR12.
  - [36] V. Avrutin, M. A. Reshchikov, N. Izyumskaya, R. Shimada, S.W. Novak, and H. Morkoç, "Effect of thermal annealing on deep and near-band edge emission from ZnO films grown by plasma-assisted MBE", be published in Mat. Res. Soc. Symp. Proc., vol. 1109.
  - [37] A. Sanchez-Juarez, A. Tiburcio-Silver, A. Ortiz, E.P. Zironi, and J. Rickards, "Electrical and optical properties of fluorine-doped ZnO thin films prepared by spray pyrolysis", Thin Solid Films, vol. 333, no. 1-2, pp. 196-202, Nov. 1998.
  - [38] H.Y. Xu, Y.C. Liu, R. Mu, C.L. Shao, Y.M. Lu, D.Z. Shen, and X.W. Fan, "F-doping effects on electrical and optical properties of ZnO nanocrystalline films", Appl. Phys. Lett., vol. 86, no. 12, pp. 123107-1 - 123107-3, Mar. 2005.
  - [39] E. Chikoidze, M. Nolan, M. Modreanu, V. Sallet, and P. Galtier, "Effect of chlorine doping on electrical and optical properties of ZnO thin films", Thin Solid Films, vol. 516, no. 22, pp. 8146-8149, Sep. 2008.
  - [40] D. C. Look, B. Claflin, and H. E. Smith, "Origin of conductive surface layer in annealed ZnO", Appl. Phys. Lett., vol. 92, no. 12, pp. 122108-1 - 122108-3, Mar. 2008.
  - [41] M. Keever, T.J. Drummond, H. Morkoç, K. Hess, B.G. Streetman, and M. Ludowise, "Hall-effect and mobility in heterojunction layers", J. Appl. Phys., vol. 53, no. 2, pp. 1034-1036, Feb. 1982.
  - [42] B. Claflin, D. C. Look, S. J. Park, and G. Cantwell; "Persistent n-type photoconductivity in p-type ZnO", J. Crystal Growth, vol. 287, no. 1, pp. 16-22, Jan. 2006.
  - [43] C.H. Park, S.B. Zhang, and S.H. Wei, "Origin of p-type doping difficulty in ZnO: The impurity perspective", Phys. Rev. B, vol. 66, no. 7, pp. 073202-1-3, Aug. 2002.
  - [44] D.C. Look and B. Claflin, "High-quality, melt-grown ZnO single crystals", Phys. Status Solidi B, vol. 241, no. 3, 624-630, Mar. 2004.
  - [45] M.G. Wardle, J. P. Goss, and P. R. Briddon, "Theory of Li in ZnO: A limitation for Li-based p-type doping", Phys. Rev. B, vol. 71, no. 15, pp. 155205-1-10, Apr. 2005.
  - [46] Y.J. Zeng, Z.Z. Ye, W.Z. Xu, D.Y. Li, J.G. Lu, L.P. Zhu, B.H. Zhao, "Dopant source choice for formation of p-type ZnO:Li acceptor", Appl. Phys. Lett., vol. 88, no. 6, pp. 062107-1-3, Feb. 2006.
  - [47] S.S. Lin, J.G. Lu, Z.Z. Ye, H.P. He, X.Q. Gu, L.X. Chen, J.Y. Huang, and B.H. Zhao, "p-Type behavior in Na-doped ZnO films and ZnO homojunction light-emitting diodes", Sol. State Commun. vol. 148, no. 1-2, pp. 25-28, Oct. 2008.
  - [48] S.S. Lin, Z.Z. Ye, J.G. Lu, H.P. He, L.X. Chen, X.Q. Gu, J.Y. Huang, L.P. Zhu, and B.H. Zhao, "Na doping concentration tuned conductivity of ZnO films via pulsed laser deposition and electroluminescence from ZnO homojunction on silicon substrate", J. Phys. D, vol. 41, no.15, pp. 155114-1 - 155114-6, Aug. 2008.
  - [49] Y.F. Yan, M.M. Al-Jassim, and S.-H. Wei, "Doping of ZnO by group-IB elements", Appl. Phys. Lett., vol. 89, no. 18, pp. 181912-1-3, Oct. 2006.
  - [50] E. Mollwo, G. Müller, and P. Wagner, "Energy position of Cu acceptor level in ZnO monocrystals", Sol. St. Comm., vol. 13, no. 8, pp. 1283-1287, Aug. 1973.
  - [51] H.S. Kang, B.D. Ahn, J.H. Kim, G.H. Kim, S.H. Lim, H. W. Chang, and S.Y. Lee, "Structural, electrical, and optical properties of p-type ZnO thin films with Ag dopant", Appl. Phys. Lett., vol. 88, no. 20, pp. 202108-1-3, May 2006.

- [52] L. Duan, W. Gao, R. Chen, and Z. Fu, "Influence of post-annealing conditions on properties of ZnO:Ag films", *Sol. State Commun.*, vol. 145, no. 9-10, pp. 479-481, Mar. 2008.
- [53] F. Reuss, C. Kirchner, T. Gruber, R. Kling, S. Maschek, W. Limmer, A. Waag, and P. Ziemann, "Optical investigations on the annealing behavior of Ga and gallium- and nitrogen-implanted ZnO", *J. Appl. Phys.*, vol. 95, no. 7, pp. 3385-3390, Apr. 2004.
- [54] B.K. Meyer, J. Sann, D.M. Hofmann, C. Neumann, and A. Zeuner, "Shallow donors and acceptors in ZnO", *Semicond. Sci. Technol.*, vol. 20, no. 4, pp. S62-S66, Apr. 2005.
- [55] S. Limpijumrong, X. Li, S.-H. Wei, and S. B. Zhang, "Substitutional diatomic molecules NO, NC, CO, N<sub>2</sub>, and O<sub>2</sub>: Their vibrational frequencies and effects on p doping of ZnO", *Appl. Phys. Lett.*, vol. 86, no. 21, pp. 211910-1-3, May 2005.
- [56] C. L. Perkins, Lee S H, Li X N, Asher S E and Coutts T J, "Identification of nitrogen chemical states in N-doped ZnO via x-ray photoelectron spectroscopy", *J. Appl. Phys.*, vol. 97, no. 3, pp. 034907-1-7, Feb. 2005.
- [57] Z.-Z. Ye, J.-G. Lu, H.-H. Chen, Y.-Z. Zhang, L. Wang, B.-H. Zhao, and J.-Y. Huang, "Preparation and characteristics of p-type ZnO films by DC reactive magnetron sputtering", *J. Crystal Growth*, vol. 253, no. 1-4, pp. 258-264, Jun. 2003.
- [58] J.G. Lu, Y.Z. Zhang, Z.Z. Ye, L. Wang, B.H. Zhao, and J.Y. Huang, "p-type ZnO films deposited by DC reactive magnetron sputtering at different ammonia concentrations", *Mater. Lett.*, vol. 57, no. 22-23, pp. 3311-3314, Jul. 2003.
- [59] C.-C. Lin, S.-Y. Chen, S.-Y. Cheng, and H.-Y. Lee, "Properties of nitrogen-implanted p-type ZnO films grown on Si<sub>3</sub>N<sub>4</sub>/Si by radio-frequency magnetron sputtering", *Appl. Phys. Lett.*, vol. 84, no. 24, pp. 5040-5042, Jun. 2004.
- [60] A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S.F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma, and M. Kawasaki, "Repeated temperature modulation epitaxy for p-type doping and light-emitting diode based on ZnO", *Nature Mater.*, vol. 4, no. 1, pp. 42-46, Jan. 2005.
- [61] S.V. Ivanov, A. El-Shaer, M. Al-Suleiman, A. Bakin, A. Waag, O.G. Lyublinskaya, N.M. Schmidt, S.B. Listoshin, R.N. Kyutt, V.V. Ratnikov, A.Ya. Terentyev, B.Ya. Ber, T.A. Komissarova, L.I. Ryabova, and D.R. Khokhlov, "Studies of N-doped p-ZnO layers grown on c-sapphire by radical source molecular beam epitaxy", *J. Kor. Phys. Soc.*, vol. 53, no. 5 SI, Pt. 2 SI, pp. 3016-3020, Nov. 2008.
- [62] L. G. Wang and A. Zunger, "Dilute nonisovalent (II-VI)-(III-V) semiconductor alloys: Monodoping, codoping, and cluster doping in ZnSe-GaAs", *Phys. Rev. Lett.*, vol. 90, no. 7, pp. 075205-1-8, Feb. 2003.
- [63] E.-C. Lee, Y.-S. Kim, Y.-G. Jin, and K.-J. Chang, "First-principles study of p-type doping and codoping in ZnO", *J. Korean Phys. Soc.*, vol. 39, Suppl. S, pp. S23-S26, Dec. 2001.
- [64] M. Sanmyo, Y. Tomita, and K. Kobayashi, "Preparation of zinc oxide films containing Be and N atoms by radio frequency magnetron sputtering", *Thin Solid Films*, vol. 472, no. 1-2, pp. 189-194, Jan. 2005.
- [65] A. Tsukazaki, H. Saito, K. Tamura, M. Ohtani, H. Koinuma, M. Sumiya, S. Fuke, T. Fukumura, and M. Kawasaki, "Systematic examination of carrier polarity in composition spread ZnO thin films codoped with Ga and N", *Appl. Phys. Lett.*, vol. 81, no. 2, pp. 235-237, Jul. 2002.
- [66] K. Nakahara, H. Takasu, P. Fons, A. Yamada, K. Iwata, K. Matsubara, R. Hunger, and S. Niki, "Growth of N-doped and Ga+N-codoped ZnO films by radical source molecular beam epitaxy", *J. Crystal Growth*, vol. 237-239, Pt. 1, pp. 503-508, Apr. 2002.
- [67] M. Sumiya, A. Tsukazaki, S. Fuke, A. Ohtomo, H. Koinuma, and M. Kawasaki, "SIMS analysis of ZnO films co-doped with N and Ga by temperature gradient pulsed laser deposition", *Appl. Surf. Sci.*, vol. 223, no. 1-3, pp. 206-209, Feb. 2004.
- [68] S.H. Lim, J.W. Kim, H.S. Kang, G.H. Kim, H.W. Chang, and S.Y. Lee, "Characterizations of phosphorus doped ZnO multi-layer thin films to control carrier concentration", *Superlat. Microstruct.*, vol. 38, no. 4-6, pp. 377-384, Oct.-Dec. 2005.
- [69] C.-C. Lin, S.-Y. Chen, and S.-Y. Cheng, "Physical characteristics and photoluminescence properties of phosphorous-implanted ZnO thin films", *Appl. Surf. Sci.*, vol. 238, no. 1-4, pp. 405-409, Nov. 2004.
- [70] Y.W. Heo, Y.W. Kwon, Y. Li, S.J. Pearton, and D.P. Norton, "Properties of Phosphorus-Doped (Zn,Mg)O Thin Films and Device Structures", *J. Electron. Mater.*, vol. 34, no. 4, pp. 409-415, Apr. 2005.
- [71] F.G. Chen, Z. Ye, W. Xu, B. Zhao, L. Zhu, and J. Lv, "Fabrication of p-type ZnO thin films via MOCVD method by using phosphorus as dopant source", *J. Cryst. Growth*, vol. 281, no. 2-4, pp. 458-462, Aug. 2005.
- [72] V. Vaithianathan, B.-T. Lee, and S. S. Kim, "Pulsed-laser-deposited p-type ZnO films with phosphorus doping", *J. Appl. Phys.*, vol. 98, no. 4, pp. 043519-1-4, Aug. 2005.
- [73] D.-K. Hwang, H.-S. Kim, J.-H. Lim, J.-Y. Oh, J.-H. Yang, S.-J. Park, K.-K. Kim, D. C. Look, and Y. S. Park, "Study of the photoluminescence of phosphorus-doped p-type ZnO thin films grown by radio-frequency magnetron sputtering", *Appl. Phys. Lett.*, vol. 86, no. 15, pp. 151917-1-3, Apr. 2005.
- [74] S.-H. Kang, D.-K. Hwang, and S.-J. Park, "Low-resistance and highly transparent Ni/indium-tin oxide ohmic contacts to phosphorous-doped p-type ZnO", *Appl. Phys. Lett.*, vol. 86, no. 21, pp. 211902-1-3, May 2005.
- [75] D. C. Look, G. M. Renlund, R. H. Burgener, II, and J. R. Sizelove, "As-doped p-type ZnO produced by an evaporation/sputtering process", *Appl. Phys. Lett.*, vol. 85, no. 22, pp. 5269-5271, Nov. 29 2004.
- [76] V. Vaithianathan, B.-T. Lee, and S. S. Kim, "Preparation of As-doped p-type ZnO films using a Zn<sub>3</sub>As<sub>2</sub>/ZnO target with pulsed laser deposition", *Appl. Phys. Lett.*, vol. 86, no. 6, pp. 062101-1-3, Feb. 2005.
- [77] U. Wahl, E. Rita, J.G. Correia, A.C. Marques, E. Alves, and J.C. Soares, "Direct Evidence for As as a Zn-Site Impurity in ZnO", *Phys. Rev. Lett.*, vol. 95, no. 21, pp. 215503-1-4, Nov. 2005.
- [78] T.S. Jeong, M.S. Han, J.H. Kim, C.J. Youn, Y.R. Ryu, H.W. White, "Crystallinity-damage recovery and optical property of As-implanted ZnO crystals by post-implantation annealing", *J. Crystal Growth*, vol. 275, no. 3-4, pp. 541-547, Mar. 2005.
- [79] S.-J. So and C.-B. Park, "Diffusion of phosphorus and arsenic using ampoule-tube method on undoped ZnO thin films and electrical and optical properties of P-type ZnO thin films", *J. Crystal Growth*, vol. 285, no. 4, pp. 606-612, Dec. 2005.
- [80] T. Aoki, Y. Shimizu, A. Miyake, A. Nakamura, Y. Nakanishi, and Y. Hatanaka, "p-Type ZnO Layer Formation by Excimer Laser Doping", *Phys. Stat. Sol. (b)*, vol. 229, no. 2, pp. 911-914, Jan. 2002.
- [81] F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, and J. L. Liu, "High-mobility Sb-doped p-type ZnO by molecular-beam epitaxy", *Appl. Phys. Lett.*, vol. 87, no. 15, pp. 152101-1-3, Oct. 2005.
- [82] F. X. Xiu, Z. Yang, L. J. Mandalapu, D. T. Zhao, and J. L. Liu, "Photoluminescence study of Sb-doped p-type ZnO films by molecular-beam epitaxy", *Appl. Phys. Lett.*, vol. 87, no. 25, pp. 252102-1-3, Dec. 2005.
- [83] Y. W. Heo, Y. W. Kwon, Y. Li, S. J. Pearton, and D. P. Norton, "P-type behavior in phosphorus-doped (Zn,Mg)O device structures", *Appl. Phys. Lett.*, vol. 84, no. 18, pp. 3474-3476, May 2004.
- [84] Y. J. Li, Y. W. Heo, Y. Kwon, K. Ip, S. J. Pearton, and D. P. Norton, "Transport properties of p-type phosphorus-doped (Zn,Mg)O grown by pulsed-laser deposition", *Appl. Phys. Lett.*, vol. 87, no. 7, pp. 072101-1-3, Aug. 2005.
- [85] D. P. Norton, M. Ivill, Y. Li, Y. W. Kwon, J. M. Erie, H. S. Kim, K. Ip, S. J. Pearton, Y. W. Heo, S. Kim, B. S. Kang, F. Ren, A. F. Hebard, and J. Kelly, "Charge carrier and spin doping in ZnO thin films", *Thin Solid Films*, vol. 496, no. 1, pp. 160-168, Feb. 2006.
- [86] S. Limpijumrong, S. B. Zhang, S.-H. Wei, and C. H. Park, "Doping by Large-Size-Mismatched Impurities: The Microscopic Origin of Arsenic or Antimony-Doped p-Type Zinc Oxide", *Phys. Rev. Lett.*, vol. 92, no. 15, 155504-1-4, Apr. 2004.
- [87] W.-J. Lee, J. Kang, K.J. Chang, "Electronic structure of phosphorus dopants in ZnO", *Physica B*, vol. 376, pp. 699-702, Apr. 2006.
- [88] Y.R. Ryu, T.S. Lee, and H.M. White, "Properties of arsenic-doped p-type ZnO grown by hybrid beam deposition", *Appl. Phys. Lett.*, vol. 83, no. 1, pp. 87-89, Jul. 2003.
- [89] F.X. Xiu, Z. Yang, L.J. Mandalapu, J.L. Liu, and W. P. Beyermann, "p-Type ZnO films with solid-source phosphorus doping by molecular-beam epitaxy", *Appl. Phys. Lett.*, vol. 88, no. 5, pp. 052106-1-3, Jan. 2006.



- [90] M. Kawasaki (Tohoku University, Sendai, Japan), communication at MRS2008 Fall Meeting.
- [91] Norton (University of Florida, Gainesville, FL, USA), communication at MRS 2008 Fall Meeting.
- [92] Y.R. Ryu, T.S. Lee, J.A. Lubguban, H.W. White, B.J. Kim, Y.S. Park, and C.J. Youn, "Next generation of oxide photonic devices: ZnO-based ultraviolet light emitting diodes", *Appl. Phys. Lett.*, vol. 88, no. 24, pp. 241108-1-3, Jun. 2006.
- [93] Y.R. Ryu, J.A. Lubguban, T.S. Lee, H.W. White, T.S. Jeong, C.J. Youn, and B.J. Kim, "Excitonic ultraviolet lasing in ZnO-based light emitting devices", *Appl. Phys. Lett.*, vol. 90, no. 13, pp. 131115-1-3, Mar. 2007.
- [94] S. Chu, J.H. Lim, L.J. Mandalapu, Z. Yang, L. Li, and J.L. Liu, "Sb-doped p-ZnO/Ga-doped n-ZnO homojunction ultraviolet light emitting diodes", *Appl. Phys. Lett.*, vol. 92, no. 15, pp. 152103-1-3, Apr. 2008.
- [95] S.Chu, M. Olmedo, Z. Yang, J.Y. Kong, J.L. Liu, "Electrically pumped ultraviolet ZnO diode lasers on Si", *Appl. Phys. Lett.*, vol. 93, no. 18, pp. 181106-1-3, Nov. 2008.
- [96] A. Dadgar, A. Krtischil, F. Bertram, S. Giemisch, T. Hempel, P. Veit, A. Diez, N. Oleynik, R. Clos, J. Christen, and A. Krost, "ZnO MOVPE growth: From local impurity incorporation towards p-type doping", *Superlat. Microstruct.*, vol. 38, no. 4-6, pp. 245-255, Oct. 2005.
- [97] A. Krtischil, A. Dadgar, N. Oleynik, J. Bläsing, A. Diez, and A. Krost, "Local p-type conductivity in zinc oxide dual-doped with nitrogen and arsenic," *Appl. Phys. Lett.*, vol. 87, no. 26, 262105-1-3, Dec. 2005.
- [98] A. Krtischil, A. Dadgar, A. Diez, and A. Krost, "Electrical characterization of defect states in local conductivity domains in ZnO:NAs layers", *J. Mat. Res.*, vol. 22, no. 7, pp. 1775-1778, Jul. 2007.
- [99] J.-L. Zhao, X.M. Li, A. Krtischil, A. Krost, W.D. Yu, Y.-W. Zhang, Y.-F. Gu, and X.-D. Gao, "Study on anomalous high p-type conductivity in ZnO films on silicon substrate prepared by ultrasonic spray pyrolysis", *Appl. Phys. Lett.*, vol. 90, no. 6, pp. 062118-1-3, Feb. 2007.
- [100] S.H. Wei, "Overcoming the doping bottleneck in semiconductors", *Computational Materials Science*, vol. 30, no. 3-4, pp. 337-348, Aug. 2004.
- [101] H. Kato, M. Sano, K. Miyamoto, and T. Yao, "High-quality ZnO epilayers grown on Zn-face ZnO substrates by plasma-assisted molecular beam epitaxy", *J. Crystal Growth*, vol. 265, no. 3-4, pp. 375-381, May 2004.
- [102] A. El-Shaer, A. Bakin, A.Che. Mofor, J. Stoimenos, B. Pecz, A. Waag, "Layer by layer growth of ZnO on (0001) sapphire substrates by radical-source molecular beam epitaxy", *Superlat. Microstruct.*, vol. 42, no. 1-6, pp. 158-164, Jul. 2007.
- [103] J. Chevallier, W.C. Dautremont-Smith, C.W. Tu, and S.J. Pearton, "Donor neutralization in GaAs(Si) by atomic hydrogen", *Appl. Phys. Lett.*, vol. 47, No. 2, pp. 108-110, Jul. 1985.
- [104] J.M.Dallesasse, I. Szafrank, J.N. Baillargeon, N. El-Zein, N. Holonyak, Jr., G.E. Stillman, and K.Y. Cheng, "Hydrogenation of Si- and Be-doped InGaP," *J. Appl. Phys.*, vol. 68, no. 11, pp. 5866-5870, Dec. 1990.
- [105] D. Seghier, J.T. Gudmundsson, and H.P. Gislason, "Hydrogen passivation of nitrogen-related energy levels in ZnSe and ZnS<sub>0.5</sub>Se<sub>0.5</sub> grown by MBE", *Physica B*, vol. 273-274, pp. 891-894, Dec. 1999.
- [106] T. Yasuda, T. Yasui, B.P. Zhang, and Y. Segawa, "Direct observation of nitrogen acceptor passivation in ZnSe by hydrogen plasma," *J. Crystal Growth*, vol. 159, no. 1-4, pp. 1168-1170, Feb. 1996.
- [107] J.W. Lee, S.J. Pearton, J.C. Zolper, and R.A. Stall, "Hydrogen passivation of Ca acceptors in GaN," *Appl. Phys. Lett.*, vol. 68, no. 15, pp. 2102-2104, Apr. 1996.
- [108] J. Neugebauer and C. G. van de Walle, "Hydrogen in GaN – novel aspects of a common impurity", *Phys. Rev. Lett.*, vol. 75, no. 24 pp. 4452-4455, Dec. 1995.
- [109] Y.F. Yan, S.B. Zhang, S.J. Pennycook, and S.T. Pantelides, "A theoretical study of p-type doping of ZnO: problems and solutions", in *Mater. Res. Soc. Symp. Proc.*, vol. 666, F2.6, 2001.
- [110] Y.Z. Zhang, J.G. Lu, L.L. Chen, and Z.Z. Ye, "Properties of N-doped ZnO thin films in annealing process", *Sol. State Commun.*, vol. 143, no. 11-12, pp. 562-565, Sep. 2007.
- [111] J.G. Lu, and S. Fujita, "Hydrogen-assisted nitrogen-acceptor doping in ZnO", *Phys. Stat. Sol. (a)*, vol. 205, no. 8, pp. 1975-1977, Aug. 2008.
- [112] Y.F. Yan, S.B. Zhang, and S.T. Pantelides, "Control of doping by impurity chemical potentials: Predictions for p-type ZnO", *Phys. Rev. Lett.*, Vol. 86, no. pp. 5723-5726, Jun. 2001.
- [113] W.Z. Xu, Z.Z. Ye, Y.J. Zeng, L.P. Zhu, B.H. Zhao, L. Jiang, J.G. Lu, H.P. He, and S.B. Zhang, "ZnO light-emitting diode grown by plasma-assisted metal organic chemical vapor deposition", *Appl. Phys. Lett.*, vol. 88, no. 17, pp. 173506-1-3, Apr. 2006.
- [114] S.Z. Sun, G.S. Tompa, B. Hoerman, D.C. Look, B.B. Claflin, C.E. Rice, and P. Masaun, "Metalorganic chemical vapor deposition and characterization of ZnO materials", *J. Electron. Mat.*, vol. 35, no. 4, pp. 766-770, Apr. 2006.
- [115] J. Li, S.-H. Wei, S.-S. Li, and J.-B. Xia, "Design of shallow acceptors in ZnO: First-principles band-structure calculations", *Phys. Rev. B*, vol. 74, no. 8, pp. 081201R-1-4, Aug. 2006.
- [116] Y.F. Yan, J. Li, S.-H. Wei, and M. M. Al-Jassim, "Possible approach to overcome the doping asymmetry in wideband gap semiconductors", *Phys. Rev. Lett.*, vol. 98, no. 13, pp. 135506-1-4, Mar. 2007.



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